National Defence / Défense nationale

DEVELOPMENT OF A NEW APPARATUS FOR TESTING CANISTERS AGAINST PHOSGENE

by

B.H. Harrison, R. Poirier, B. Zanette
and F. Villeneuve

DEFENCE RESEARCH ESTABLISHMENT OTTAWA
TECHNICAL NOTE 84-16

Canada

October 1984
Ottawa

National Defence / Défense nationale

DEVELOPMENT OF A NEW APPARATUS FOR TESTING CANISTERS AGAINST PHOSGENE

by

B.H. Harrison, R. Poirier, B. Zanette
and F. Villeneuve
Materials Section
Protective Sciences Division

DEFENCE RESEARCH ESTABLISHMENT OTTAWA
TECHNICAL NOTE 84-16

PCN
13B30

October 1984
Ottawa

ABSTRACT

A new apparatus for testing gas mask canisters against phosgene has been developed. Test procedures are described in detail.

RÉSUMÉ

Un nouvel appareil de vérification de l'efficacité des cartouches de masque à gaz contre le phosgène a été mis au point. Le présent article décrit en détail la méthode d'essai de ces cartouches.

1. INTRODUCTION

During the manufacture of C1 and C2 canisters quality control tests are required to ensure that the canisters are being manufactured correctly. One of the tests that is required is a means to assess the integrity of the charcoal bed. The test developed for this purpose employs phosgene and measures the service life of the canister. This test is ideal for the purpose and compared to other less volatile agents provides a rapid test which is suitable for quality control purposes.

A phosgene canister test apparatus was developed at DREO many years ago (1) and has been used since then both at the canister manufacturers facilities and at DREO for this purpose. In that apparatus air and phosgene were metered through rotameters, mixed, the concentration checked by wet chemical methods, and adjustments made until the correct concentration was achieved.

Recently a requirement was established by the LCMM (2) to develop a modern canister test apparatus employing modern methods and technology. At the same time under the auspices of TTCP Subgroup E's Focus Officers to Advise on Charcoal Test Methods, and Action Group 19, international agreement was reached on standardized test conditions. For phosgene it was agreed that the test conditions would be:

Challenge Concentration	20,000 mg/m^3
Air Flow	30 ℓ/min
Temperature	25 $\pm$ 3°C
Relative Humidity	15%
Canister Pre-Conditioning	moisture content less than 5%
Effluent Breakpoint	4 mg/m^3

Although sophisticated gas-sampling techniques are being used in this laboratory (3) to plot the effluent concentration versus time and establish the exact time when the concentration reached 4 mg/m^3, it has been found that in practice the effluent concentration rises very rapidly and a simple detector paper which produces a colour change at a concentration close to 4 mg/m^3 is much easier to use and is quite acceptable for quality control purposes.

A new canister test apparatus was therefore developed, the operation of which will be described in detail. The new equipment employs mass flow controllers which automatically meter under controlled conditions the air and phosgene. The controllers are extremely stable and provide a constant challenge to the canisters for long periods of time and eliminate the need for frequent calibration checks. This has removed the need for most of the routine wet chemical analysis and significantly simplifies the

operation of the new equipment. The new equipment has also been designed to be modular and can be used in any fume hood which has adequate ventilation.

2. SAFETY MEASURES

Because of the high toxicity of phosgene all operators of the equipment must be fully aware of its chemical and toxicological properties before using the equipment.

Phosgene is a colourless, nonflammable, highly toxic gas with an odor like that of musty hay. It is readily liquified to a light yellow liquid. The liquid has a specific gravity of 1.38 and the vapour density is 3.41 with respect to air.

Phosgene is a strong lung irritant and causes severe damage to the alveoli of the lungs. This is followed by edema, resulting in asphyxiation. Inhalation of phosgene produces catching of the breath, choking, immediate coughing, tightness of the chest, lacrimation, difficulty and pain in breathing and cyanosis. Serious symptoms may not develop until several hours following exposure, for the immediate symptoms produced by even a fatal dose may be relatively mild since phosgene elicits no marked respiratory reflexes. Thus, a person who appears to be but slightly affected immediately after exposure may become a casualty several hours later. The most pronounced symptoms of phosgene poisoning are coughing with bloody sputum and weakness which may last for months (4).

Phosgene is ten times more toxic than chlorine. A concentration of 500 mg/m^3 is lethal after an exposure of ten minutes. An atmosphere of 80 mg/m^3 can cause lung injuries and exposure to an atmosphere containing 100 mg/m^3 for as little as 30 minutes is very dangerous. A person aquainted with phosgene's odor can detect 2 mg/m^3, a concentration of 4 mg/m^3 is readily noticeable, and a concentration of 8 mg/m^3 is moderately strong.

Adequate ventilation is a necessity for all work with phosgene. The canister test apparatus should be used in a fume hood with good air flow characteristics and a face velocity of at least 28 m/min (100 ft/min).

Personnel using phosgene should be aware of the hazards associated with it and procedures should be established to handle

accidents. Protective masks should be available for all personnel working with, and in the vicinity of, the phosgene. Because cylinders of phosgene can be purchased with and without an 'inductor' tube, personnel should be familiar with cylinder markings which identify the inductor tube.

3. GENERAL DESCRIPTION OF THE APPARATUS

Figure 1 shows a schematic diagram of the apparatus and the flow paths for air and phosgene. In the system, controlled flows of dry air and phosgene are provided by the flow sensors [1] and [3] and control valves [2] and [4] respectively. They are then mixed in the chamber [6] before challenging the canister screwed into the test chamber [7]. The effluent from the canister passes through the detector tube [8], into which a detector paper is hung, and through a second canister [9] which removes any phosgene from the airstream which has passed through the test canister before being vented into the fume hood.

Provision has also been made for ports to sample the challenge mixture of air and phosgene [10] and for leak testing [11] to ensure that the test canister is screwed securely into the apparatus. Figure 2 is a photograph of the apparatus.

4. DETAILS OF COMPONENT PARTS

4.1 DRY AIR SUPPLY

A supply of compressed air with a relative humidity less than 15% is required for testing the canisters. Although dry air can be supplied by a number of methods the one chosen for use on the equipment at DREO employs a pressure swing air dryer (sometimes referred to as a heatless dryer) which runs continuously and does not need to be regenerated like the

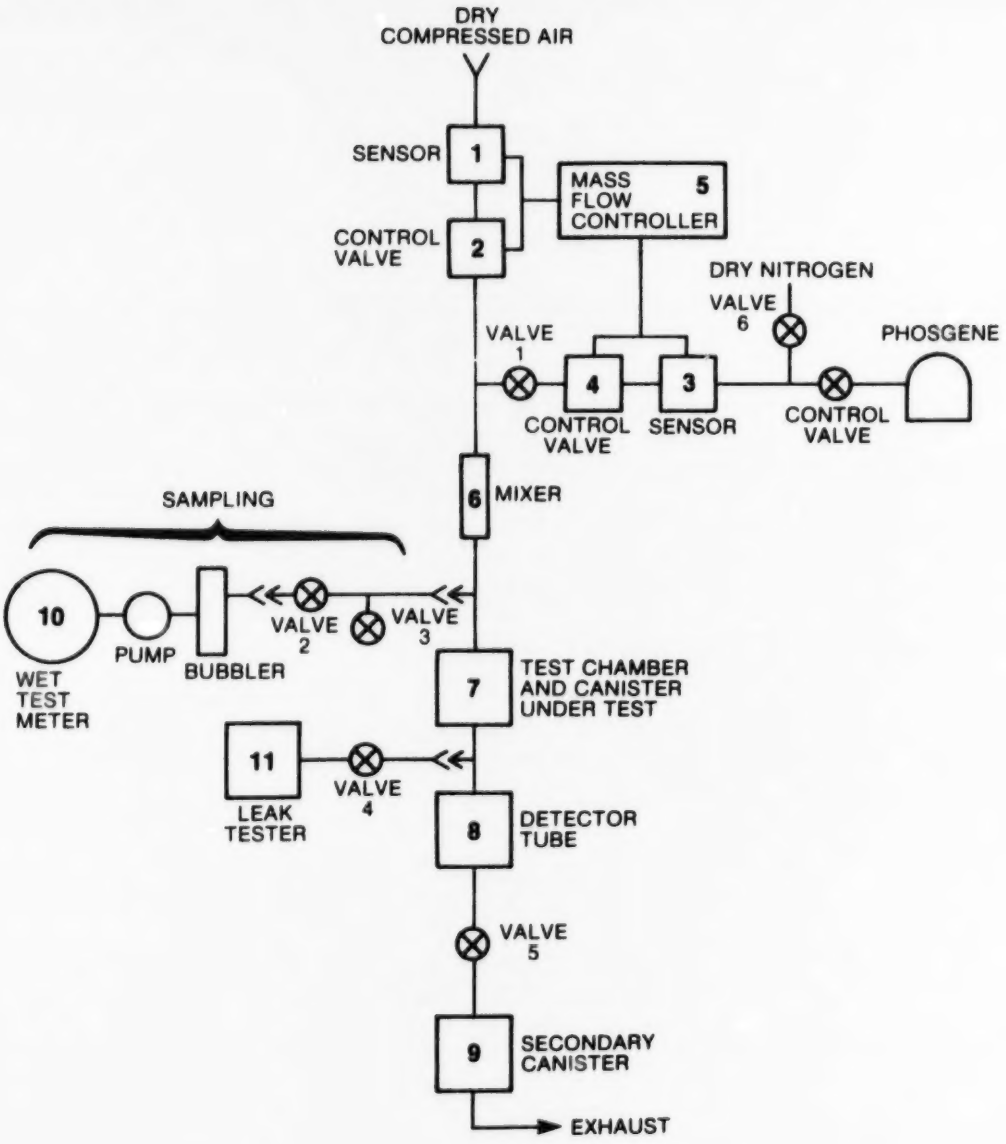

Figure 1. Schematic

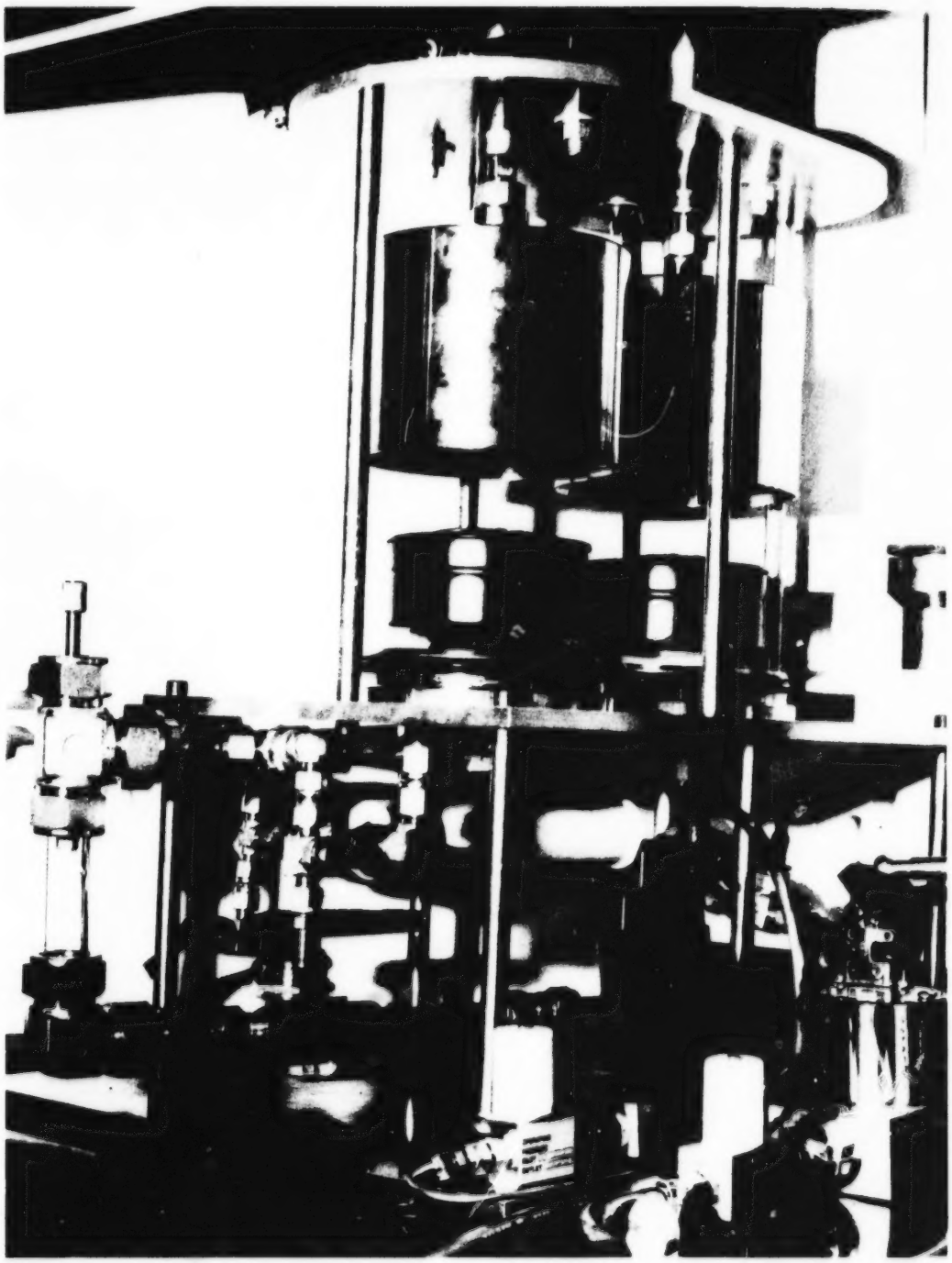

Figure 2: Photograph of Test Apparatus.

earlier ones used at DREO for this purpose (1). The relative humidity of the air can be checked continuously by placing a humidity sensor in the dry air supply line or checked at intervals by attaching the humidity sensor to the exhaust air from the test apparatus.

Because the pressure swing air dryers provide a reliable souce of dry air the latter system has been used at DREO. A Norgen Model 1-109-A032 air dryer and a Hygrocon Humidity Sensor (Physical Chemical Research, NY) are currently being used on the apparatus to provide dry air and monitor the relative humidity.

4.2 MASS FLOW CONTROLLERS

A Matheson Model 8249 Mass Flow Controller is used to control and monitor the flow of air (0-50 ℓ/min) and phosgene (0-300 mℓ/min) in the apparatus. This type of controller has been found to be very reliable and requires only a periodic check on its calibration. The reader is referred to the operating manual for the mass flow controller for further details of its operation and use. An in-line filter should be installed between the gas supplies and the mass flow controllers to prevent small particles entering the sensing elements.

4.3 PHOSGENE SUPPLY

As mentioned previously cylinders of phosgene can be ordered with or without an inductor tube. For this type of testing they should be ordered <u>without</u> the inductor tube. The cylinder can be connected to the mass flow controller using a simple control valve (no regulator required) and stainless steel tubing.

4.4 MIXER

To ensure complete mixing of the air and phosgene a mixer was developed which consists of a series of baffles inside a teflon tube (5). A photograph of this assembly can be found in Figure 3.

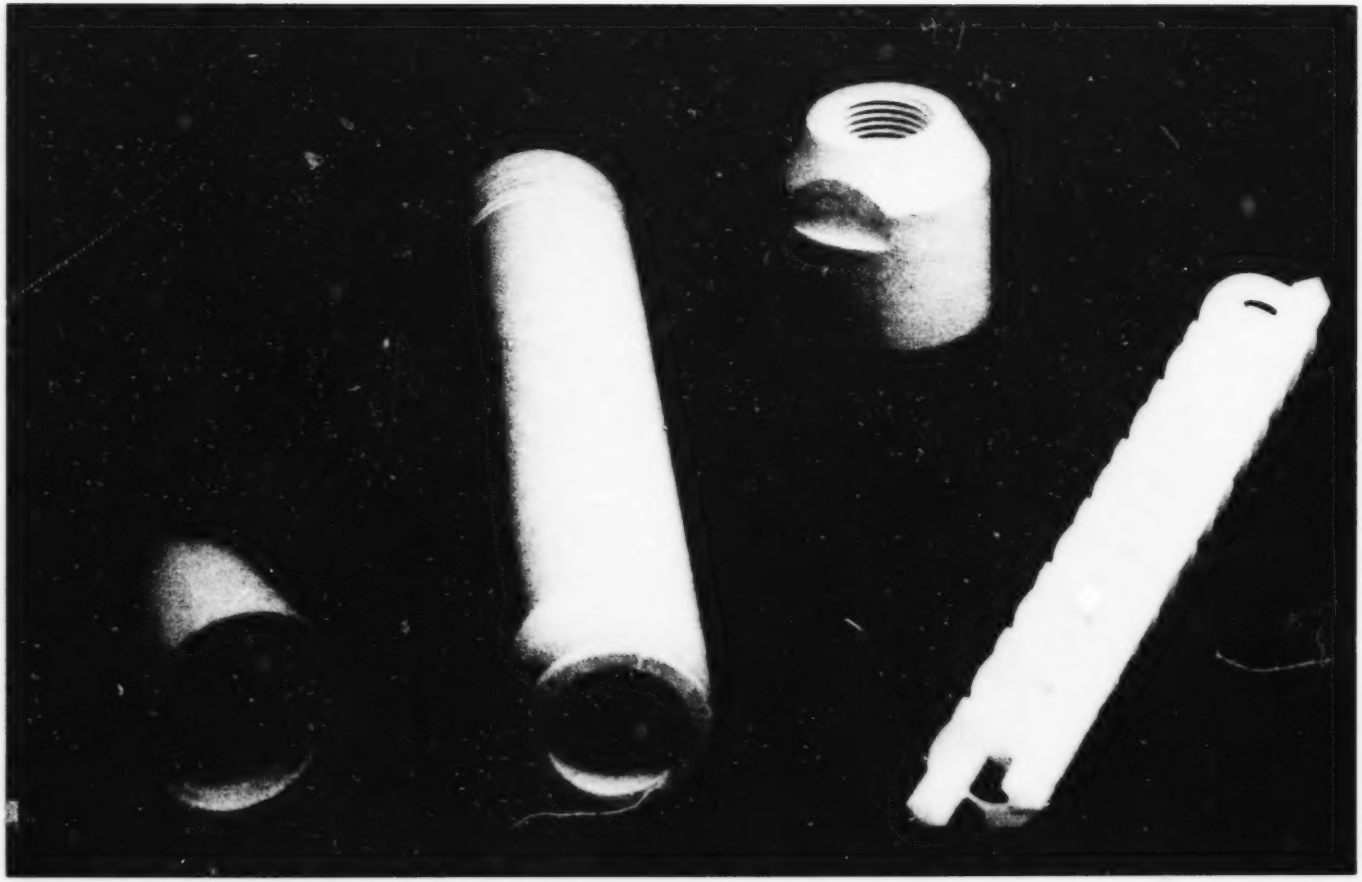

Figure 3: Photograph of Mixer.

4.5 TEST CHAMBER

A stainless steel test chamber has been developed (6) and can be seen in Figure 4. Access into the chamber to replace canisters is accomplished by actuating a pneumatic cylinder which lifts the upper section of the test chamber (cf Figure 4). An 'O'-ring is used to seal the two sections together when the chamber is closed.

4.6 DETECTOR TUBE

In order to measure the time when the phosgene begins to penetrate through the canister a test paper is inserted into the air flow which changes colour when it comes into contact with phosgene. The detector paper is held on the end of a small clamp in a transparent plastic tube (7). Figure 5 is a photograph of this assembly.

4.7 SAMPLING

A schematic diagram of the apparatus used to sample the air/phosgene mixture in order to establish the phosgene concentration can be found in Figure 1. Basically the air/phosgene mixture was drawn out of the apparatus by a small pump. The phosgene in the mixture was trapped in the absorbent bubbler and the quantity of air drawn out of the apparatus was recorded on the wet test meter. Further details of the absorbent bubbler can be found in the earlier report (1).

4.8 LEAK TESTER

In order to establish that the canister under test had been successfully sealed into the apparatus a leak test was required. The apparatus used was similar to that described earlier (1).

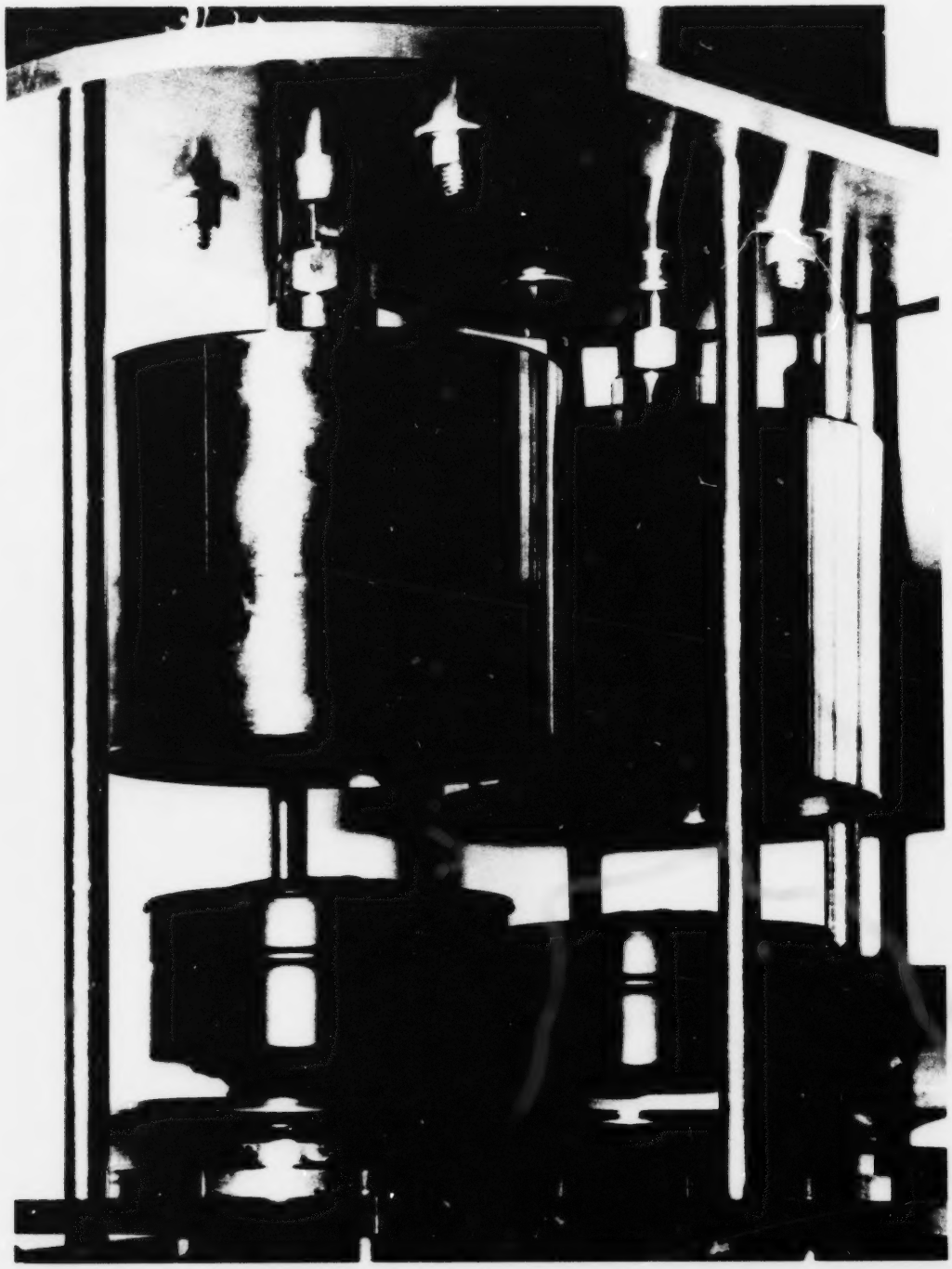

Figure 4: Test Canister.

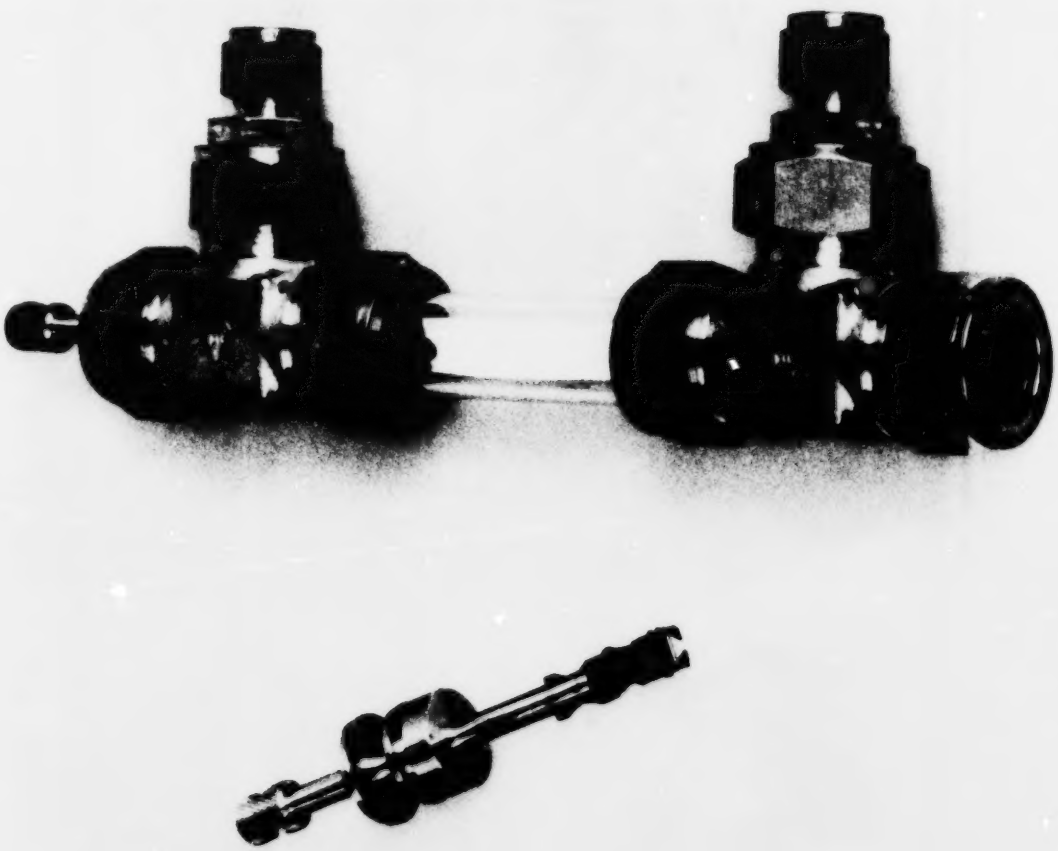

Figure 5: Detector Tube.

5. PREPARATION OF TEST PAPERS, INDICATOR SOLUTION AND ABSORBING SOLUTION

Both the phosgene absorbing solution and the indicator papers described below were used when testing canisters with phosgene. The test procedures can be found in Section 6-8.

5.1 TEST PAPERS (HARRISON'S REAGENT)

Test papers were prepared by dipping filter papers (Whatman No. 50) in a solution of:

5 g paradimethylaminobenzaldehyde and
5 g diphenylamine dissolved in
100 mℓ 95% ethyl alcohol.

The papers were dried in a chlorine-free atmosphere and then cut into strips approximately 1.5 × 5 cm. They are sensitive to light and must be stored in a stoppered, brown bottle.

Test papers prepared as above are capable of detecting phosgene in concentrations of less than 4 mg/m^3. If stored in a darkened bottle in a chlorine-free atmosphere, they were stable for several months.

5.2 INDICATOR SOLUTION

Ferric alum solution was used as an indicator in the KCNS-$AgNO_3$ titration (section 7.2). It was prepared by dissolving 10 g $FeNH_4(SO_4)_2$ in 90 mℓ H_2O and 1.5 mℓ HNO_3.

5.3 ABSORBING SOLUTION

The phosgene absorbing solution was prepared by dissolving:

20 g sodium hydroxide and
40 g hexamethylenetetramine in
1 litre of distilled water.

This solution could be stored for several weeks without deteriorating.

6. CALIBRATION OF THE EQUIPMENT

6.1 CALIBRATION PROCEDURE FOR AIR FLOW

(1) Screw a canister into each of the chambers and then close them.

(2) Turn on the mass flow controller.

(3) Adjust the mass flow controller for the air to give approximately 30 ℓ/min.

(4) Connect the flow of air exiting the apparatus to a dry test meter.

(5) Measure the air flow using the dry test meter.

(6) Adjust the mass flow controller setting until the air flow is 30 ℓ/min.

(7) Note the setting required and lock in place.

6.2 CALIBRATION PROCEDURE FOR PHOSGENE FLOW

(1) Adjust the air flow to 30 ℓ/min (cf 6.1).

(2) Open the control valve on the phosgene cylinder.

(3) Open valve 1 (cf. Figure 1).

(4) Set the phosgene mass flow controller so that it delivers 136 mℓ/min (based on manufacturers calibration, cf Section 7.4).

(5) Sample the air/phosgene mixture as described in Section 7 and determine the phosgene concentration.

(6) Readjust the phosgene setting until the concentration is 20,000 ± 500 mg/m^3.

(7) Note the setting and lock in place.

(8) Close the control valve on the phosgene cylinder.

(9) Flush the phosgene out of the line using dry nitrogen introduced by opening valve 6 with the mass flow controller (phosgene) operating.

(10) Close valve 6.

7. CHALLENGE (PHOSGENE) CONCENTRATION

7.1 PROCEDURE FOR MEASURING PHOSGENE CONCENTRATION

(1) Fill the absorbent bubbler (cf Figure 1) with 50 mℓ of absorbing solution (cf Section 5.3).

(2) Connect the bubbler to the canister test apparatus and the wet test meter [10].

(3) Turn on the phosgene mass flow controller at the required setting and allow 2-3 minutes for the system to stabilize.

(4) Purge the dead space in the sampling line by opening valve 3 for 2-3 seconds and then close it.

(5) Open valve 2 until approximately 2ℓ of air has passed through the absorbent bubbler (approximately 5 min).

(6) Close valve 2.

(7) Note how much air passed through the wet test meter.

(8) Use the analytical procedure in Section 7.2 to determine the phosgene concentration.

7.2 ANALYTICAL PROCEDURE

(1) Take the absorbent bubbler off the apparatus and blow the absorbing solution carefully through the influent end of the bubbler into a 250 mℓ beaker using compressed air applied to the effluent spherical joint.

(2) Wash the contents of bubbler into a beaker with two 50 mℓ aliquots of 10% HNO_3.

(3) Add 15.0 mℓ of 0.1 N Ag NO_3.

(4) Filter and wash the residue three times with 25 mℓ aliquots of distilled water, using a suction flask, Millipore funnel and a No. 1 Whatman filter paper (or equivalent).

(5) Add 1.0 mℓ ferric alum solution and 0.5 mℓ nitrobenzene to the filtrate.

(6) Back titrate with 0.1N KCNS to a faint pink endpoint while mixing with a magnetic stirrer.

(7) Record the endpoint and determine the phosgene concentration using the procedure in Section 7.3.

7.3 CALCULATION OF PHOSGENE CONCENTRATION

To determine the phosgene concentration in the test chamber during the test, a fixed volume (V litres) of the air-gas was bubbled through the absorbing solution. The solution was analyzed for phosgene using $AgNO_3$ and KCNS.

The weight of phosgene present was determined using the following formula:

$$W\ (mg) = (M_1N_1 - M_2N_3) \times 49.46$$

where M_1 = volume of $AgNO_3$ (mℓ)
M_2 = volume of KCNS (mℓ)
N_1 = normality of $AgNO_3$
N_2 = normality of KCNS
49.46 = gram equivalent weight phosgene.

The phosgene concentration in the sample of volume V is:

$$C = \frac{W}{V} = \frac{49.46(M_1N_1 - M_2N_2)}{V}\ mg/\ell$$

7.4 REQUIRED FLOW RATE FOR PHOSGENE

The following are flow details for phosgene which allow the initial flow controller setting to be established in Section 6.2.

Challenge concentration	20,000 mg/m^3
Air Flow	30 ℓ/min
Phosgene requirement	600 mg/min
Phosgene flow	136 mℓ/min

If the transducer used has a maximum capacity of 300 mℓ/min (i.e. 100%) then the setting for 136 mℓ/min

$$= \frac{136}{300} \times 100 = 45.3\%$$

8. CANISTER TEST PROCEDURE

(1) Install the canister to be tested in the test chamber.

(2) Conduct a leak test by:

(a) Putting a rubber plug into the top of the canister.
(b) Closing valve 5.
(c) Opening valve 4 to the leak tester and checking for leaks.

(3) If leaks are present establish their source.

(4) If no leaks are present close valve 4, open valve 5, and remove the rubber plug from the canister.

(5) Install a new detector paper in the detector tube.

(6) Close the test chamber.

(7) Check that the air mass flow controller is set to provide 30 ℓ/min and turn it on.

(8) Open the control valve on the phosgene cylinder (if not already open).

(9) Open valve 1.

(10) Check that the phosgene mass flow controller is set to generate a concentration of 20,000 mg/m^3.

(11) Turn the phosgene mass flow controller on and at the same time start a timer.

(12) Observe the detector paper. The test is complete when the first perceptible tint of yellow is observed in the detector paper.

(13) Note the time when the colour change is noted.

(14) Turn the phosgene mass flow controller off.

(15) Close valve 1.

(16) Wait 2-3 minutes before opening the test chamber and removing the canister.

(17) Mutilate the thread on the canister so that it cannot be accidentally used again.

(18) If further canisters are to be tested start again at step 1.

(19) If no further canisters are to be tested close the control valve on the phosgene cylinder and flush the phosgene line with dry nitrogen by opening valve 6.

9. DISPOSAL OF CANISTERS

Canisters which have been tested with phosgene should be stored in a fume hood until they are disposed of. Disposal is accomplished by piercing the sides of the canister, inside a well ventilated fume hood, and pouring the charcoal into water, thus hydrolyzing the adsorbed phosgene.

10. MAINTENANCE

The equipment has been designed to operate efficiently for long periods of time with little or no maintenance. However the equipment should be routinely checked for leaks using a leak detector such as Snoop* and the 'O' ring seal on the test chamber kept lubricated with grease. It is also advisable to keep spare seals, seats and orifice plates for the mass flow controllers.

---

* Regd. trade name.

11. REFERENCES

1. R.W. Nolan and C.J. Wellington, Defence Research Establishment Ottawa Technical Note 70-10, April 1970.

2. Task DLAEEM 82.

3. B.H. Harrison and R. Poirier, Defence Research Establishment Ottawa Report No. 868, September 1983.

4. Effects of Exposure to Toxic Gases - First Aid and Medical Treatment, W. Braker, A. Mossman and d. Siegel, Matheson, Lyndhurst, N.J.

5. Defence Research Establishment Drawing No. 3385.

6. Defence Research Establishment Drawing No. 3332.

7. Defence Research Establishment Drawing No. 3534.

UNCLASSIFIED
security Classification

DOCUMENT CONTROL DATA - R & D
(Security classification of title, body of abstract and indexing annotation must be entered when the overall document is classified)

1. ORIGINATING ACTIVITY
Defence Research Establishment Ottawa
Department of National Defence
Ottawa, Ontario, Canada K1A 0Z4

2a. DOCUMENT SECURITY CLASSIFICATION
UNCLASSIFIED

2b. GROUP

3. DOCUMENT TITLE
DEVELOPMENT OF A NEW APPARATUS FOR TESTING CANISTERS AGAINST PHOSGENE

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)
TECHNICAL NOTE

5. AUTHOR(S) (Last name, first name, middle initial)
HARRISON, Brian H., POIRIER, Robert, ZANETTE, Bruno and VILLENEUVE, Frank

6. DOCUMENT DATE	7a. TOTAL NO OF PAGES	7b. NO OF REFS
OCTOBER 1984	18	7

8a. PROJECT OR GRANT NO	9a. ORIGINATOR'S DOCUMENT NUMBER(S)
	DREO TECHNICAL NOTE 84-16
8b. CONTRACT NO	9b. OTHER DOCUMENT NO (S) (Any other numbers that may be assigned this document)

10. DISTRIBUTION STATEMENT
UNLIMITED DISTRIBUTION

11. SUPPLEMENTARY NOTES	12. SPONSORING ACTIVITY

13. ABSTRACT

A new apparatus for testing gas mask canisters against phosgene has been developed. Test procedures are described in detail.

DSIS
77-065

UNCLASSIFIED
Security Classification

KEY WORDS

ADSORPTION
ACTIVATED CARBON
CHARCOAL
CANISTERS
PHOSGENE
CHEMICAL WARFARE AGENTS

INSTRUCTIONS

1. ORIGINATING ACTIVITY: Enter the name and address of the organization issuing the document.

2a. DOCUMENT SECURITY CLASSIFICATION: Enter the overall security classification of the document including special warning terms whenever applicable.

2b. GROUP: Enter security reclassification group number. The three groups are defined in Appendix 'M' of the DRB Security Regulations.

3. DOCUMENT TITLE: Enter the complete document title in all capital letters. Titles in all cases should be unclassified. If a sufficiently descriptive title cannot be selected without classification, show title classification with the usual one-capital-letter abbreviation in parentheses immediately following the title.

4. DESCRIPTIVE NOTES: Enter the category of document, e.g. technical report, technical note or technical letter. If appropriate, enter the type of document, e.g. interim, progress, summary, annual or final. Give the inclusive dates when a specific reporting period is covered.

5. AUTHOR(S): Enter the name(s) of author(s) as shown on or in the document. Enter last name, first name, middle initial. If military, show rank. The name of the principal author is an absolute minimum requirement.

6. DOCUMENT DATE: Enter the date (month, year) of Establishment approval for publication of the document.

7a. TOTAL NUMBER OF PAGES: The total page count should follow normal pagination procedures, i.e., enter the number of pages containing information.

7b. NUMBER OF REFERENCES: Enter the total number of references cited in the document.

8a. PROJECT OR GRANT NUMBER: If appropriate, enter the applicable research and development project or grant number under which the document was written.

8b. CONTRACT NUMBER: If appropriate, enter the applicable number under which the document was written.

9a. ORIGINATOR'S DOCUMENT NUMBER(S): Enter the official document number by which the document will be identified and controlled by the originating activity. This number must be unique to this document.

9b. OTHER DOCUMENT NUMBER(S): If the document has been assigned any other document numbers (either by the originator or by the sponsor), also enter this number(s).

10. DISTRIBUTION STATEMENT: Enter any limitations on further dissemination of the document, other than those imposed by security classification, using standard statements such as:

(1) "Qualified requesters may obtain copies of this document from their defence documentation center."

(2) "Announcement and dissemination of this document is not authorized without prior approval from originating activity."

11. SUPPLEMENTARY NOTES: Use for additional explanatory notes.

12. SPONSORING ACTIVITY: Enter the name of the departmental project office or laboratory sponsoring the research and development. Include address.

13. ABSTRACT: Enter an abstract giving a brief and factual summary of the document, even though it may also appear elsewhere in the body of the document itself. It is highly desirable that the abstract of classified documents be unclassified. Each paragraph of the abstract shall end with an indication of the security classification of the information in the paragraph (unless the document itself is unclassified) represented as (TS), (S), (C), (R), or (U).

The length of the abstract should be limited to 20 single-spaced standard typewritten lines; 7½ inches long.

14. KEY WORDS: Key words are technically meaningful terms or short phrases that characterize a document and could be helpful in cataloging the document. Key words should be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context.